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"Crystal Growth in Substrate-Confined Liquids"

TECHNICAL REPORT

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SUMMARY

→ The task objective is to develop crystal growth techniques utilizing substrate-confined liquids. Crystals are to be grown as arrays of single crystals of materials relevant to photodetection.

The main technical problem remaining is to further develop techniques which have worked for the growth of Ge and InSb crystals, since attempts to grow CdTe crystals directly have proved too difficult due to the volatility of both components of that compound. The further development is focused on improving yields in the several processing steps performed in series on these materials.

→ The basic approach is experimental and utilizes vacuum evaporation, chemical vapor deposition, and related techniques as well as optical, SEM and x-ray instrumentation.

→ The main result obtained is that arrays of single crystals can be grown with a basal plane oriented parallel to the substrate for the materials: In, Ge, InSb, in order of decreasing perfection.

This result is important as a basis for the growth of the desired crystal arrays, though yields must be improved to make the process attractive.



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DETAILED REPORT

The most extensive experiments have been conducted with indium metal; this material is also the most amenable of those studied to the processing steps needed to produce arrays of single crystals. The main work with indium is described in Part I of this report. Part II briefly describes experiments to grow germanium arrays by CVD of germane over the indium arrays of Part I.

Part I: Indium Crystallization from Substrate-Confined Liquid

Crystallization of thin films has received renewed interest the past few years largely due to developments utilizing *liquid* thin films[†]. Zone melting produced by laser or other energy beams is by far the most intensely studied method, but an approach employing isothermally heated substrates is possible as well. In the latter case, liquid is stably confined in the substrate surface by the combined effects of surface tension and geometry^{††}. A particularly favorable example is provided by a SiO_2 substrate surface, containing concavities with vertical sidewalls, to confine a liquid such as In which forms a contact angle near 90° against the substrate. This example is treated in the present discussion.

The metal In studied here is not likely to lead to applications in itself, but may be a suitable beginning from which one can learn to grow semiconductor crystals such as the In pnictides in a similar manner. A recent exploratory study^{*} dealt with solution growth of Ge from substrate-confined

[†] Representative examples of contemporary work appear in Abstracts 142-162, J. Electrochem. Soc., 129 (1982) 99c-101c.

^{††} T. F. Kuech and J. O. McCaldin, Appl. Phys. Lett. 37 (1980) 44.

^{*} T. F. Kuech and J. O. McCaldin, Thin Solid Films, 97 (1982) 9.

Au-Ge liquid, and In may similarly be a suitable solvent. A further possibility is stoichiometric growth of the semiconducting In compounds. The easiest of these to deal with experimentally is InSb, a material of considerable interest for infrared detection. In such an application one would like to utilize arrays of crystals, such as was discussed recently*.

The first step toward the application just mentioned is to produce arrays of substrate-confined In with suitable control of purity, wetting, and distribution over the substrate. The experiments described here show that these goals may be attained and that, in the course of doing so, arrays of crystals with strong preferred orientation are produced.

A. Experimental Method

Amorphous substrates suitable for the present experiments were obtained by oxidizing (100) or (111) Si wafers. Concavities were needed in such substrates to contain liquid In for crystallization and were produced by conventional lithography with a single mask. The mask contained arrays of triangular, square or hexagonal openings from which concavities with vertical sidewalls were developed on the substrate by plasma etching. The size of a concavity was typically on the order of 10 μm in diameter and 4 or 7 μm in depth. Chip size was typically $5 \times 5 \text{ mm}^2$.

The flow chart in Table I indicates sample processing steps for the two types of substrates used, labeled sparsely-packed and densely-packed. In the case of sparsely-packed substrates, the width of the region between concavities, i.e. the field, was 5 to 8 μm . The oxide remaining on the field was removed by HF and then the entire surface was oxidized again to a thickness of $\sim 900 \text{ \AA}$ or sometimes $\sim 1700 \text{ \AA}$. The substrate was cleaned by O_2 plasma just before deposition. Indium was deposited by vacuum evaporation with substrate

* T. F. Kuech and J. O. McCaldin, Thin Solid Films, 97 (1982) 9.

TABLE I. Process Steps.

A. Sparsely-Packed Substrate	B. Densely-Packed Substrate
<p>SiO₂ on (100) Si Plasma etch Remove oxide Oxidize entire surface Deposit In Planarize Clear field Anneal</p>	<p>SiO₂ on (111) Si Plasma etch Chemical etch Remove oxide Oxidize entire surface Deposit In Clear field Anneal</p>

near room temperature at a rate of $\sim 1 \mu\text{m}/\text{min}$ to a thickness of 2 to 4 μm , using 99.999% purity In and Mo evaporation boat. Base pressure measured at ion pump was 10^{-6} Torr $\sim 10^{-4}$ Pa. The deposited In was planarized by drawing a razor blade lightly across the surface, leaving concavities filled with In. A small amount of In remaining on the field was removed by dilute HNO₃.

Densely-packed substrate was fabricated by additional enlargement of concavity after plasma etching. A mixture of 2% HF, 80% HNO₃ and 18% acetic acid was used for this purpose, resulting in thin walls of 0.5 to 1 μm between concavities. After the same processing as described above, In was deposited on the substrate heated slightly higher than the melting point of In (156°C) to a thickness sufficient to fill concavities. That resulted in a big droplet of In in each concavity and a lot of small droplets of In on the field. These small droplets were removed chemically by the mixture of 1cc HF, 2cc H₂O₂ and 100cc H₂O.

Specimens with concavities filled with In and cleared fields, were then put into furnace at 800°C for 15 min in forming gas (13% H₂ in He) to deoxidize the In and allow it to form equilibrium shapes in the concavities. For the

first 1 to 2 min of this annealing, the forming gas was bubbled through deionized water, to give a $\frac{[H_2O]}{[H_2]}$ ratio of ~ 0.20 , and passed the specimen at a velocity of ~ 2.6 cm/s. The cooling rate was 3 to $10^\circ\text{C}/\text{min}$ near the melting point of In. The processes of deposition through annealing were sometimes iterated to get a good filling of In in concavities.

X-ray analyses of specimens were made by both diffractometer and Laue methods. Diffractometer measurements to detect any preferred orientation parallel to the substrate utilized monochromatic $\text{Cu}_{K\alpha}$ radiation. Laue patterns were produced with unfiltered Mo radiation at a variety of accelerating voltages, but in most cases at 10 kV so that most of the x-ray absorption occurred in the overlying In layer rather than in the Si substrate.

B. Results

Appearance of specimens at various stages of processing is illustrated in the accompanying SEM pictures. When annealing was performed with *dry* forming gas only, rather poor wetting of In to the SiO_2 surface typically occurred as shown in Fig. 1. This figure shows a sparsely-packed array of hexagonal concavities with the field cleared, concavities substantially underfilled, and In tending to form hemispherical shapes instead of lying flat. The underfilling was a common consequence of using an etching step to clear the field, and, together with poor wetting, led to the hemispherical shapes. Poor wetting is evidenced in the figure by droplets not flowing freely on the sidewalls of concavities. Elsewhere on such specimens one occasionally observed two droplets contacting each other but not fusing, and also droplets on the field which presented an elliptical shape when viewed from directly above instead of the circular shape expected at equilibrium. An average contact angle between In and SiO_2 observed for many such specimens is $\sim 110^\circ$.

An In array in densely-packed concavities is shown in Fig. 2. Appearance of the specimen immediately after In deposition onto the heated substrate, Fig. 2(a), shows that fusion of In droplets has led to one large droplet in each concavity and much smaller droplets on top of the thin walls, as expected^{**}. Taking advantage of this disparity in size of In droplets, droplets on the field, which have a small contact area with substrate, can be easily removed by the diluted mixture of HF and H₂O₂, which causes droplets to become detached from the substrate. Subsequent annealing in forming gas including the wet H₂ step resulted in the substrate wetting shown in Fig. 2(b). In this case the contact angle is close to 90°, indicating improved wetting between metal and substrate. The occasional surface wrinkling evident in the figure, however, suggests impurities may be present at some surface regions. Figure 2(b) also demonstrates a commonly-observed retraction of In from the sidewalls, as if shrinkage associated with solidification were concentrated there.

In specimens processed through the wet H₂ anneal, many concavities exhibited a facet such as is shown in Fig. 3. The facet in this figure is particularly evident because of a concavity geometry which caused the In droplet to assume a convex shape. Examination of many such facets by Nomarski interference indicated that most of them are flat as far as can be detected and lie closely parallel to the substrate surface.

Also visible in Fig. 3 is a straight line traversing the contained In including the facet. Commonly the In in a concavity would exhibit a single such straight line, possibly a twin plane related to cooling stresses; In is known to deform readily by twinning. Occasionally, however, In in the concavity would show one or more curved lines in addition to the single straight line, and

^{**} J. O. McCaldin and T. F. Kuech, J. Appl. Phys. 52 (1981) 803.

these may be ordinary grain boundaries. Etching with various reagents commonly used to delineate grain boundaries in In did not reveal any additional such features.

Diffraction measurements exhibited only the In (101) and (202) peaks, indicating In (101) to be parallel to the plane of the substrate. The full-width at half maximum of these peaks was typically $\sim 0.2^\circ$ in the 2θ plot, even though the x-ray beam was incident on an array of some 10,000 concavities. Sensitivity was such that if a second orientation parallel to the substrate were present at one-tenth the strength of the (101) peak it would have been easily detected. No such second orientation was observed. Laue back reflection patterns indicated only the presence of the Si substrate. Exposures at 10 kV accelerating voltage were made for as long as 48 hours, but no spots or rings associated with the In overlay could be detected.

C. Discussion and Conclusions

These experiments show that In can be placed selectively, and uniformly, into the concavity-portion of a SiO_2 surface, and that the In can be made to wet the surface uniformly with a contact angle near 90° . The uniform wetting depends on chemical processing likely to oxidize various impurities, e.g. C, in addition to reducing any oxides of In. Once such conditions are obtained and allow the In to wet the substrate uniformly, further considerations permit one to confine In to the concavities in a uniform way. For example, in deposition onto a hot substrate with a densely-packed array of concavities, the deposition is terminated before fusion of In among neighboring concavities occurs; this usually means just filling, i.e. not overfilling, the concavities. Schemes for clearing the field depend on the surface geometry of substrate and deposited material. Indium is a soft metal and is easy to flow mechanically, e.g. scraping by razor blade.

Planarizing by razor blade is suitable for sparsely-packed substrates which have concavities covering less than 50% of the surface area. A small amount of thin In film remaining on the field is easily removed by a light chemical etching, which however causes some loss of In in concavities. In the case of densely-packed arrays, a hot substrate technique, also called** "simultaneous deposition and liquefaction", followed by etching suffices to clear the field.

Purity of both substrate and In metal is substantially improved by including a wet as well as a dry step during H_2 annealing. This treatment lowers the contact angle and produces uniform wetting. Still a problem, however, is contamination at certain areas, evidenced for example by surface wrinkling. This may be a consequence of the low H_2O concentration permissible to keep In deoxidized near $156^\circ C$. If so, the higher temperatures associated with stoichiometric or even solution growth of In pnictides should minimize this difficulty.

Crystallization in the In arrays shows a strong preferred orientation, with a densely-packed plane⁺⁺⁺ parallel to the substrate. Facets often appear on the top surface of the In parallel to the substrate, thus are presumably the same In densely-packed plane. However, other orientations may be at least occasionally present, judged by the occasional presence of grain boundaries in the In within a concavity. On the whole, however, if twinning is neglected, there appears to be a single In crystal in each concavity with its (101) plane parallel to the substrate but with no fixed azimuthal orientation.

Various experimental observations suggest that crystallization begins near the center of each small pool of metal, rather than near the sidewalls. The observed (101) alignment with the plane of the substrate is consistent with this

** J. O. McCaldin and T. F. Kuech, J. Appl. Phys. 52 (1981) 803.

+++ In the b.c. tetragonal unit cell, the In (101) plane. In the approximately equivalent F.C.C. sometimes used for In, this would be a (111) plane.

assumption, whereas nucleation near the sidewalls would produce a multiplicity of alignments. Furthermore, the observed retraction of In from all sidewalls examined at high magnification indicates crystallization did not begin there, but rather that this is where the last freezing occurs. Indium is known to contract $\sim 2\%$ in volume on freezing^{***}. Partly similar results in the electrocrystallization of Sn on patterned substrates have been reported⁺, though in that case some azimuthal orientation was observed, considerably weaker than the basal orientation. Azimuthal orientation may develop during growth rather than nucleation, however⁺⁺. Other models⁺⁺⁺, ^{****} for orienting crystals on patterned substrates would predict a definite orientation, including an azimuthal one, and thus do not appear directly applicable to the present results, though probably related.

Part II: Deposition of Germanium onto an Indium-Array Substrate to Grow Oriented Germanium Crystals

The array of indium-filled concavities described in Part I may be used as a suitable substrate for the selective deposition of Ge by the pyrolysis of germane. When sufficient Ge has been deposited onto the In in each concavity, the substrate may then be transferred to a H_2 anneal furnace and temperature cycled to precipitate Ge out of In solution and, on further cooling, grow a Ge

*** T. E. Faber, Introduction to the Theory of Liquid Metals, (University Press, Cambridge, 1972), p. 80.

+ L. S. Darken and D. H. Lowndes, *Appl. Phys. Lett.* 40 (1982) 954.

++ L. S. Darken (personal communication).

+++ Henry I. Smith and D. C. Flanders, *Appl. Phys. Lett.* 32 (1978) 349.

**** V. I. Klykov and N. N. Sheftal, *J. Crystal Growth*, 52 (1981) 687.

crystal in the concavity. Alternatively, it has been found, a Ge crystal can be grown directly during the germane pyrolysis. In this case, the indium present appears to serve only as a nucleating center so that later stages of Ge growth occur directly from the decomposition of the impinging germane molecules.

In either case, an important consideration is preferentiality of the pyrolysis of germane onto the In droplets as opposed to the S₁ field regions of the substrate. Lower temperatures, and, to a lesser extent, lower germane concentrations improve the preferentiality. But it is not yet clear whether deposition onto the field regions can be completely eliminated.

The Ge crystals produced in either of the regimes described in the second paragraph above show a strong preference to orient (111) basal planes parallel to the substrate. In this respect, Ge growth is similar to that of In described in Part I. However, Ge orientations have been observed only by microscopy and even here one can detect some variations from accurate parallelness with the substrate. This is to be contrasted with the In case of Part I, where parallelness to better than 0.2° was indicated by x-ray diffractometer methods. Present efforts are directed to characterizing and controlling Ge growth to the extent obtained for In.

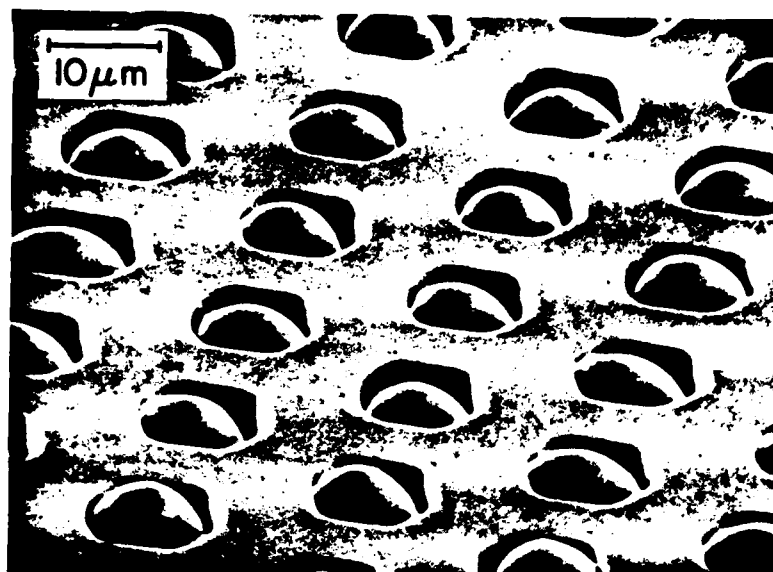


Figure 1 Indium in a sparsely-packed array of concavities. Processing is complete except that anneal was done in *dry* H₂ only. Note poor wetting of In to SiO₂ surface.

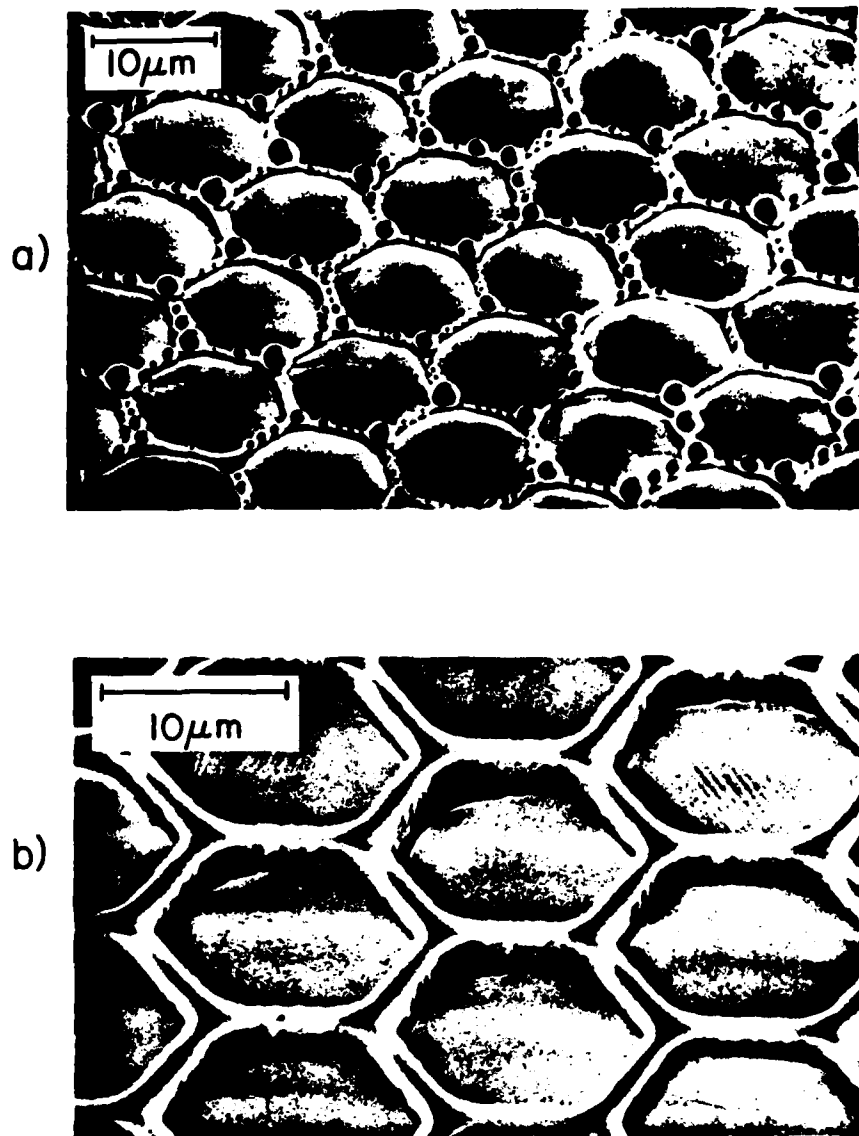


Figure 2

Indium in densely-packed array of concavities.

- (a) Processing through In deposition step. Most of the hexagonal concavities are either slightly underfilled or just filled.
- (b) After complete processing. Indium is altogether removed from the field and partly from the concavities. Wrinkled surfaces appearing in upper right-hand and lower left-hand corners suggest incomplete removal of surface contamination.

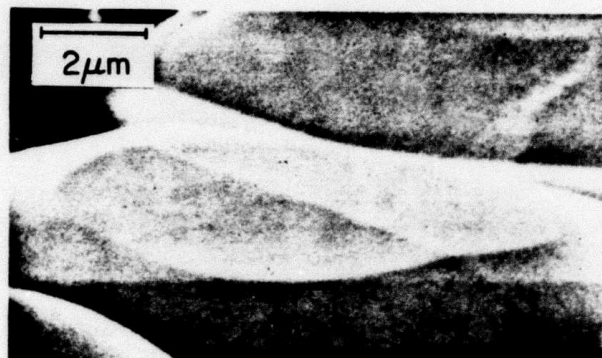


Figure 3 Facet at top of In droplet in concavity. A straight line traverses droplet, including facet, from lower right to upper left corner.